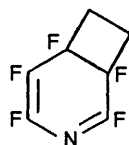


## Heterocyclic Polyfluoro-compounds. Part 29.<sup>1</sup> 2 : 1 Adducts by Photochemical Addition of Cycloalkenes to Pentafluoropyridine

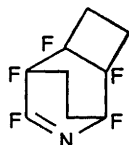
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The cyclo-alkenes, cyclo-pentene, -hexene, and *cis*-octene, each add photochemically to pentafluoropyridine to yield pairs of 2 : 1 adducts by [2 + 2] addition at C-3 and -4 and [4 + 2] addition at C-2 and -5 of pentafluoropyridine. Their stereochemistry is discussed on the basis of their physical data, and it is suggested that *endo*-addition of cyclo-pentene and -octene, and *exo*-addition of cyclohexene, is favoured for [2 + 2] addition.

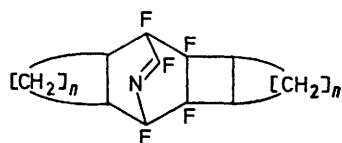
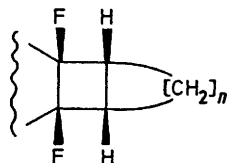
PENTAFLUOROPYRIDINE reacts photochemically with ethylene to give a 1 : 1 adduct (1), by [2 + 2] addition at C-3 and -4 of the pyridine, and a 1 : 2 adduct (2), also formed in a slow thermal [4 + 2] addition of ethylene to the adduct (1).<sup>2</sup> In this respect, it differs from pyridine



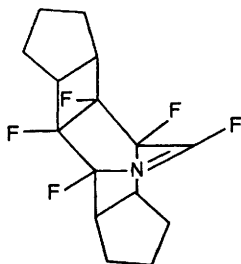
(1)



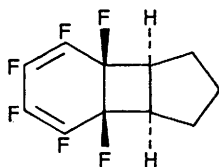
(2)

(3)  $n = 3, 4, \text{ or } 6$ 

(4)



(5)



(6)

itself, which does not undergo addition of olefins, and contrasts with benzene, where 1,3 addition of olefins is usually the favoured process.<sup>3</sup>

We here describe the reactions of pentafluoropyridine with cyclo-alkenes. Irradiation ( $\lambda > 200$  nm) of mixtures of pentafluoropyridine and a large excess of the olefins, cyclo-pentene, -hexene, and *cis*-octene, in each case leads slowly to the production of pairs of 1 : 2 adducts. No 1 : 1 adducts were obtained under these conditions, and only in the case of cyclohexene was there mass-spectrometric indication of formation of a 1 : 1 adduct in trace amounts. Their spectroscopic data (see Experimental section) indicate that the pairs of adducts are related, have the general structure (3), and pairs

are formed in the ratios 7 : 3, 4 : 5, and 4 : 1 for cyclo-pentene, -hexene, and -octene, respectively. Their detailed stereochemistry is uncertain, but we believe that the major adduct for the first and last olefin has the *cis-syn-cis* geometry (4) at the cyclobutane ring (referred to as the *endo*-isomer in the Experimental section) and the other is the corresponding *cis-anti-cis*-isomer. 1,4 Addition of the olefin from the least hindered side of the 1 : 1 adducts would then lead to the adduct (5) as the major cyclopentene adduct, and we suggest that this is the structure.

There are a number of unusual aspects to this reaction. The absence of 1 : 1 adducts is noteworthy, even when, for example, pentafluoropyridine is taken in excess with cyclopentene. Cyclohexene adds much less readily than other cycloalkenes to benzene,<sup>3</sup> whereas here it differs from the other olefins mainly in that it is the *endo*-adduct which is somewhat less favoured. Charge transfer should occur readily from the olefin to the pyridine, which would favour an 'exciplex' mechanism, which has been favoured for the addition of olefins to benzene,<sup>4</sup> and steric effects may well be important here.

There is a marked difference in the photochemistry of hexafluorobenzene and pentafluoropyridine. The benzene forms seven 1 : 1 adducts with *cis*-cyclo-octene, where the major products arise from 1,3 addition to the benzene.<sup>5</sup> Very recently it has been reported that cyclopentene forms mainly a 1 : 1 adduct (6) by [2 + 2] addition in an *anti*-fashion.<sup>6</sup>

### EXPERIMENTAL

Experimental techniques were similar to those used earlier.<sup>2</sup>

**Photochemical Additions of Pentafluoropyridine.**—(a) *With cyclopentene.* Pentafluoropyridine (2.49 g, 14.7 mmol) and cyclopentene (8.54 g, 125.6 mmol), sealed *in vacuo* in a silica ampoule (29 cm<sup>3</sup>) and the liquid phase irradiated for 200 h at a distance of 25 cm from a u.v. lamp, gave recovered reactants (10.02 g) and a solid residue (0.17 g, 0.6 mmol, 4% based upon pentafluoropyridine taken), which was sublimed at 145 °C *in vacuo* and shown by g.l.c. and n.m.r. spectroscopy to comprise two isomers of 1,2,8,9,15-pentafluoro-16-azapentacyclo[7.5.2.0<sup>2,8</sup>.0<sup>3,7</sup>.0<sup>10,14</sup>]hexadec-15-ene.

Pentafluoropyridine (23.74 g, 140.5 mmol) and cyclopentene (3.91 g, 57.5 mmol), sealed in a silica tube (300 cm<sup>3</sup>) and irradiated for 472 h, gave unchanged pentafluoropyridine (19.81 g, 117.2 mmol, 83% recovery) and cyclopentene (1.98 g, 29.1 mmol, 51% recovery), and a mixture of two

adducts (3.40 g, 11.1 mmol, 48% based upon pentafluoropyridine consumed) in the ratio 1 : 4.

Samples of each adduct were isolated by g.l.c. (2 m SE30 at 190 °C) to give the *endo*-isomer (10a) (Found: C, 58.9; H, 5.6; N, 4.6; F, 31.1.  $C_{15}H_{16}F_5N$  requires C, 59.1; H, 5.2; N, 4.6; F, 31.1%) and the *exo*-isomer (12a) (Found: C, 58.9; H, 5.2; N, 4.5; F, 31.1%), in the ratio 4 : 1.

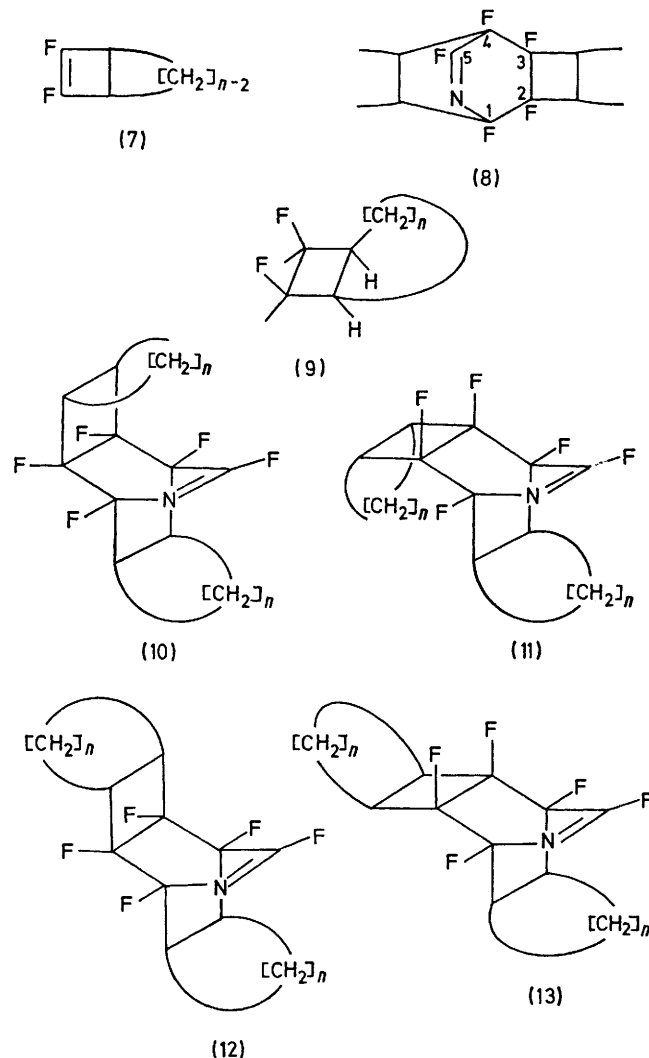
(b) *With cyclohexene*. Pentafluoropyridine (5.24 g, 31.0 mmol) and cyclohexene (9.16 g, 111.7 mmol), sealed in a silica tube (100 cm<sup>3</sup>) and the liquid phase irradiated for 308 h, gave a mixture, distilled to give unchanged reactants (11.63 g), b.p. 77–86 °C, an unstable fraction (0.25 g), b.p. 67–95 °C at 1 mmHg, which rapidly darkened and was shown by g.l.c.–mass spectrometry to be complex but possibly to contain small amounts of a 1 : 1 adduct (*m/e* 251, 232, 231, 170), and a residue, sublimed at 145 °C *in vacuo* and shown by i.r. and n.m.r. spectroscopy, and mass spectrometry, to be a 4 : 5 mixture of *endo*- (10b) and *exo*-isomers (12b) of 1,2,9,10,17-pentafluoro-18-azapentacyclo[8.6.2.0<sup>2,9</sup>.0<sup>3,8</sup>.0<sup>11,16</sup>]octadec-17-ene (2.13 g, 6.4 mmol, 21% yield based upon pentafluoropyridine taken) (Found: C, 61.1; H, 5.9; N, 4.0%;  $M^+$ , 333. Calc. for  $C_{17}H_{20}F_5N$ : C, 61.3; H, 6.0; N, 4.2%;  $M$ , 333). Unsuccessful attempts were made to separate the isomers by g.l.c.

(c) *With cyclo-octene*. Pentafluoropyridine (1.98 g, 11.7 mmol) and *cis*-cyclo-octene (10.23 g, 93.0 mmol), sealed *in vacuo* in a silica tube (22 cm<sup>3</sup>) and irradiated for 168 h, gave unchanged reactants (9.47 g), and a residue, which was sublimed at 160 °C *in vacuo* and shown by g.l.c. (2 m SE30 at 240 °C) and other physical data to be a 1 : 4 mixture of *exo*- and *endo*-isomers of 1,2,11,12,21-pentafluoro-22-azapentacyclo[10.8.2.0<sup>2,11</sup>.0<sup>3,10</sup>.0<sup>13,20</sup>]docos-21-ene (1.42 g, 3.7 mmol, 31% based upon pentafluoropyridine taken) (Found: C, 63.7; H, 7.0; N, 3.4; F, 23.7%;  $M$ , 389. Calc. for  $C_{21}H_{28}F_5N$ : C, 64.7; H, 7.2; N, 3.6; F, 24.4%;  $M$ , 389). The major isomer (12c) showed  $\nu_{\max}$  1 698 vs and the minor isomer (10c) 1 700 vs cm<sup>-1</sup> (N=CF stretch).

*Physical Properties of the Adducts*.—The mass spectra of the pairs of isomeric adducts were very similar. In Table 1 are shown selected data for the major adducts of cyclopentene and *cis*-octene, and for the mixture of cyclohexene adducts. All the adducts show a prominent molecular ion and the base peak corresponds to the olefin fragment. Particularly significant is the retro-Diels–Alder cleavage, most prominent for the cyclohexene adducts, involving loss of  $C_{n+2}H_{2n-2}F_2$  ( $n = 5, 6, \text{ or } 8$ ) corresponding to the cyclobutene (7), which is somewhat more prominent than the alternative cleavage of  $C_nH_{2n-2}$ .

The <sup>1</sup>H n.m.r. spectra of the adducts showed only absorptions corresponding to protons attached to saturated carbon atoms. In Table 2 are shown <sup>19</sup>F chemical shifts (positive

values are to low field of external CF<sub>3</sub>CO<sub>2</sub>H) for the cycloalkene adducts, where those labelled A correspond to the minor adduct for cyclopentene and -octene, and the major adduct of cyclohexene, together with those for the cor-



responding ethylene adduct. The numbering corresponds to structure (8), and corresponding absorptions were identified on the basis of similar chemical shifts, which were particularly distinctive for  $\delta(1-F)$  and  $\delta(5-F)$ , and the similarity of band envelopes, which were in general broad, complex, and ill resolved. The low-field shift  $\delta(5-F)$ , is characteristic of a CF=N grouping,<sup>7</sup> and a fluorine nucleus of

TABLE 1

Mass spectral data for cyclo-olefin–pentafluoropyridine adducts

Ion	Relative intensities (%)		
	Cyclopentene	Cyclohexene	<i>cis</i> -Cyclo-octene
$M$	11.1	19.2	12.2
$M - C_nH_{2n-3}$	6.5	13.1	7.4
$M - C_nH_{2n-2}$	1.2	5.9	1.1
$M - C_{n+2}H_{2n-2}F_2$	1.7	20.5	3.5
$C_5HF_5N$	2.3	16.2	2.1
$C_nH_{2n-2}$	100.0	100.0	100.0
$C_nH_{2n-3}$	3.9	16.3	4.6

TABLE 2

<sup>19</sup>F N.m.r. chemical shifts (p.p.m.) of olefin–pentafluoropyridine 2 : 1 adducts \*

Olefin	$\delta(1-F)$	$\delta(2-F)$	$\delta(3-F)$	$\delta(4-F)$	$\delta(5-F)$	
Ethylene	-75.1	-95.4	-107.8	-120.3	22.5	
Cyclopentene	A	-82.4	-118.9	-128.1	-126.2	31.0
	B	-80.9	-89.7	-101.4	-125.7	30.6
Cyclohexene	A	-83.7	-113.2	-121.3	-127.1	29.1
	B	-79.4	-86.1	-95.9	-124.2	30.5
<i>cis</i> -Cyclo-octene	A	-80.3	-118.8	-127.4	-123.9	28.0
	B	-77.5	-91.0	-100.3	-119.8	28.0

\* As ca. 20% solutions in CDCl<sub>3</sub>.

type CF-N is expected to absorb to low field of a fluorine of type CF-C identifying  $\delta(1-F)$ . Previously, the absorptions at  $\delta -107.8$  and  $-120.3$  p.p.m. in the ethylene adduct were tentatively assigned to 4- and 3-F, respectively.<sup>2</sup> This assignment is now reversed, since the set labelled  $\delta(3-F)$  show regular changes similar to those of the set labelled  $\delta(2-F)$ . The adducts labelled B in general showed chemical shifts much more similar to those of the ethylene adduct than those of A. We expect that the introduction of a polymethylene bridge in place of two hydrogens in the ethylene adduct would result in a substantial upfield shift of a vicinal fluorine if the dihedral angle between the C-C and C-F bonds is near zero.<sup>8</sup> The mass spectra strongly indicate the presence of a cyclobutane fragment, where the two fluorines should show such a highfield shift, if the polymethylene bridge is *cis*-(9). A *trans*-bridge is sterically improbable for the cyclopentene adducts, and the other olefin adducts appear related. The adducts A show such a high field shift of 2- and 3-F, absent from adducts B where a smaller downfield shift is observed. The fluorines 1- and 4-F in adducts A show a much smaller upfield shift, which is expected for skeleton (3) since the C-C-C-F dihedral angle will be near  $60^\circ$ . A similar but slightly smaller upfield shift [apart from  $\delta(4-F)$  for the cyclo-octene adduct] is also observed for adducts B. All the adducts show a downfield shift (5.5—8.5 p.p.m.) of 5-F, possibly as a result of some

steric compression. This suggests then the possible structures (10) or (11) for adducts B and (12) or (13) for adducts A. For addition of ethylene to pentafluoropyridine, a 1 : 1 adduct is formed as a result of [2 + 2] addition, which can add a second molecule of ethylene by [4 + 2] addition. If the same applies here, then [4 + 2] addition of the cycloalkene would suffer severe steric crowding in the transition states leading to adducts (11) and (13). Tentatively then, structures (10) and (12) are favoured for the adducts.

[9/592 Received, 18th April, 1979]

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